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The lattice contraction of nanometre-sized Sn and Bi particles produced by an electrohydrodynamic technique

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Abstract. Nanometre-sized Sn and Bi particles were produced by an electrohydrodynamic technique. The lattice parameters of the nanometre-sized Sn and Bi particles with different grain sizes were measured by x-ray diffraction. It was found that the lattice parameters a and c for the nanometre-sized Sn and Bi particles are smaller than the equilibrium lattice parameters a_0 and c_0 of the corresponding Sn and Bi perfect single crystals respectively. With a reduction in grain size, the values of a , c and the unit cell volume V decrease. The results are attributed to a supersaturation of the vacant lattice sites in the nanoscale particles.

1. Introduction

Many properties of nanocrystalline materials have been found to be essentially different from those of normal coarse-grained polycrystalline materials. This is related to the interfacial structures and ultrafine grains of the nanocrystalline materials. The interfacial structures of the nanostructured materials have been extensively investigated [1–3]. Quantitative measurements on the lattice parameters of the nanophases in the nanocrystalline Fe–Cu–Si–B [4] and Ni–P [5] alloy synthesized by crystallization of the bulk amorphous alloys, and pure Ni [6] prepared by using a JG-PF high-frequency ion beam sputtering system have revealed that the lattice structure of the nanostructured materials is changed relative to the perfect single crystal. For example, with the reduction of grain size, the lattice parameter for the Fe₂B and Ni₃P nanophases is enlarged in the a -axis and is shortened in the c -axis simultaneously, and the lattice parameter for the Ni nanophase is increased. Unstable lattice structure has been found in ultrafine particles, such as in gold particles [7] and the aluminium particles in a sandwich Al/MgO [8]. Apai *et al* [9] reported lattice contraction with decreasing particle size of Cu and Ni ultrafine particles formed by evaporating multiple layers of metal and carbon onto 500 nm polymer films. A very similar result was reported in Ni fine particles [10] prepared by the gas-evaporation technique. X-ray diffraction (XRD) measurements showed a 2.4% decrease in the lattice constant of 5 nm Ni particles.

An electrohydrodynamic (EHD) technique was utilized to produce nanometre-sized particles in the study. The nanometre-sized metal droplets disintegrated by the EHD technique solidify in flight under vacuum conditions, so almost no impurities exist in these particles, which is beneficial for studying the lattice structure of pure nanometre-sized particles. It is the aim of this paper to study the structural characteristics of the nanoscale particles and to

examine the dependence of the lattice parameters on the grain size for Sn and Bi nanometre-sized particles.

2. Experiment

Nanometre-sized Sn and Bi particle samples were prepared by means of the EHD technique. The technological process has been reported previously [11]. The metals used are high-purity Sn (99.999%) and Bi (99.999%) materials. Small pieces were placed in a quartz jet tube, sealed up and placed in the heater. When the vacuum in the chamber reached 10^{-5} Torr, the metal was heated to about 440 °C for Sn and 470 °C for Bi, and the molten metal was delivered to the tip of the capillary nozzle to which a high voltage was applied. Charged liquid droplets were formed, which were scattered and accelerated by the electric field onto a collector. The droplets solidified in flight to produce the nanometre-sized particles. A series of experimental Sn or Bi particles with various grain sizes was obtained by modifying the technological conditions [11]. The grain sizes of Sn and Bi particles were measured experimentally by means of XRD spectroscopy and transmission electron microscopy (TEM). Lattice parameter measurements were carried out using an x-ray diffractometer (Rigaku DMAX/2400) with Cu K α radiation.

3. Experimental results

Figure 1 shows the XRD spectrum of nanometre-sized Sn particles. It can be seen from figure 1 that the nanoscale Sn sample consists of only crystalline Sn phase with a tetragonal structure. Figure 2 shows the XRD spectrum of nanometre-sized Bi particles. It can be noticed from figure 2 that the nanoscale Bi sample consists of only crystalline Bi phase with a rhombohedral structure. The diffraction lines (312) for Sn and (202) for Bi are chosen to calculate the mean grain sizes of the nanoscale Sn and Bi samples respectively according to the Scherrer equation from the half-maximum width of the diffraction line after removing the instrumental broadening. The (312) XRD lines of three Sn samples are plotted in figure 3. It can be seen that all the XRD lines are broadened and all the peak positions deviate from the equilibrium value. Moreover, the deviation increases with a decrease in the grain size of the Sn sample. The (202) XRD lines of three Bi samples are plotted in figure 4: the results are similar.

The lattice parameters of the nanoscale Sn and Bi samples are determined from the peak positions of the XRD line broadening using Bragg's law:

$$2d \sin \theta_{hkl} = \lambda \quad (1)$$

where d is the interplanar spacing, θ_{hkl} the diffraction angle of the (hkl) diffraction plane and λ the wavelength of the Cu K α radiation. The lattice parameters of the nanometre-sized Sn particles can be determined using the peak positions of the (101), (301) and (312) lines. Those of the nanometre-sized Bi particles can be determined using the peak positions of the (202), (116) and (122) lines. The lattice parameters for the Sn perfect single crystal are $a_0 = 0.5831$ nm and $c_0 = 0.3182$ nm; those for the Bi perfect single crystal are $a_0 = 0.4546$ nm and $c_0 = 1.1860$ nm. Tables 1 and 2 list the values of a , c and V in Sn and Bi particles respectively with different grain sizes. In table 1, the maximum standard errors of a and c are 0.000 09 and 0.000 07 nm respectively. In table 2, the maximum standard errors of a and c are 0.000 09 and 0.000 38 nm respectively. For Sn, the values of a and c in the nanometre-sized particles are always smaller than a_0 and c_0 respectively and decrease simultaneously with a reduction in grain size. For Bi, the lattice parameters a and c are

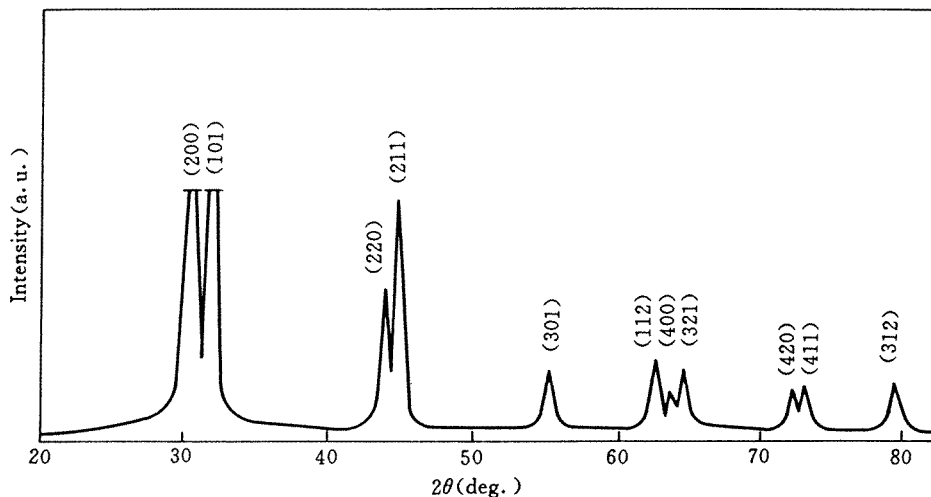


Figure 1. XRD spectrum of nanometre-sized Sn particles.

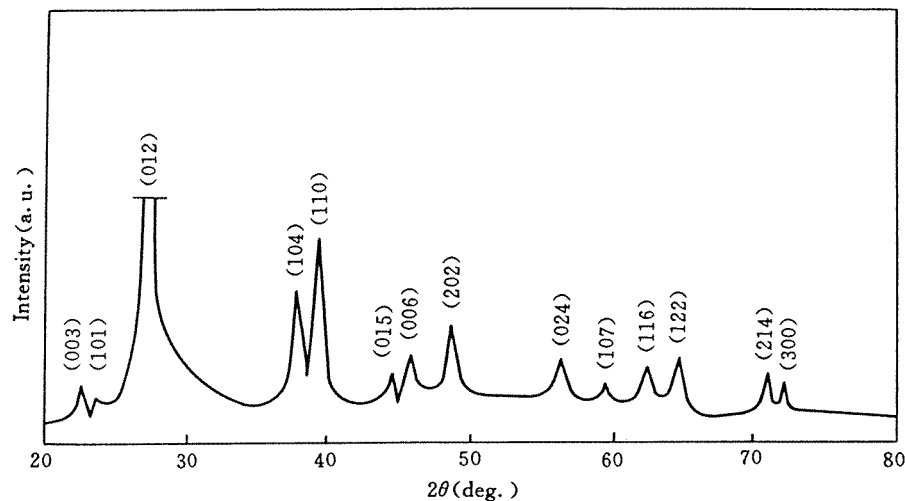


Figure 2. XRD spectrum of nanometre-sized Bi particles.

also below a_0 and c_0 respectively and have more reduced values with decreasing grain size. Normal polycrystalline Sn and Bi were analysed using the same x-ray diffractometer. The results show that the lattice parameters of normal polycrystalline Sn are $a = 0.58310$ nm and $c = 0.31831$ nm, and those of normal polycrystalline Bi are $a = 0.45473$ nm and $c = 1.18609$ nm. The standard errors are the same as above. Therefore, the measured values of a and c for the normal polycrystalline Sn and Bi basically conform to the standard values a_0 and c_0 for Sn and Bi perfect single crystals.

We use $\Delta a/a_0$ ($\Delta a = a - a_0$) and $\Delta c/c_0$ ($\Delta c = c - c_0$) to represent the deviation of the lattice parameters of the nanometre-sized Sn and Bi samples from the equilibrium values. Figures 5 and 6 show the variation of lattice distortions $\Delta a/a_0$ and $\Delta c/c_0$ with the mean grain size for nanometre-sized Sn and Bi particles respectively. It can be seen from figure 5 that all

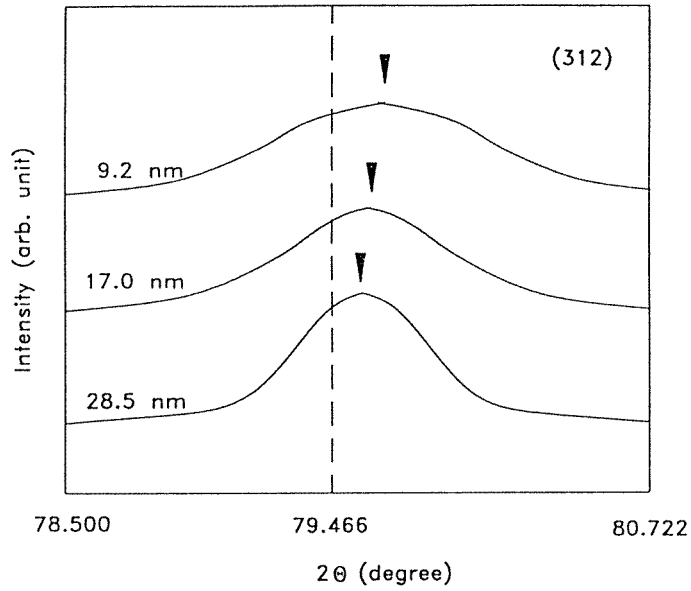


Figure 3. The positions of XRD lines of nanometre-sized Sn particles with different grain sizes for the (312) plane.

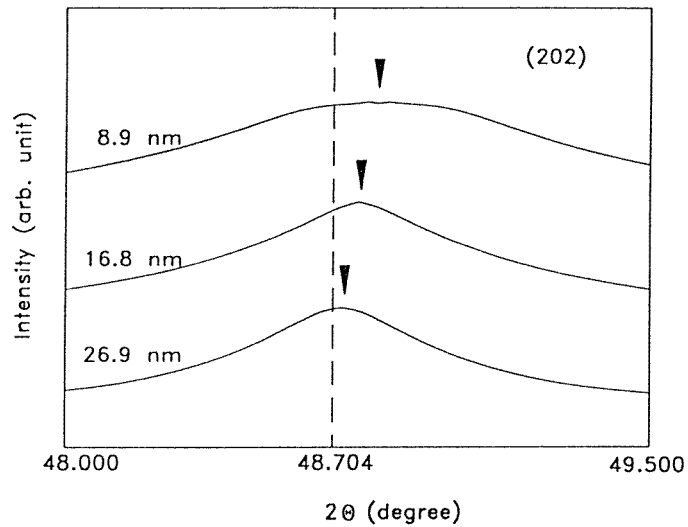


Figure 4. The positions of XRD lines of nanometre-sized Bi particles with different grain sizes for the (202) plane.

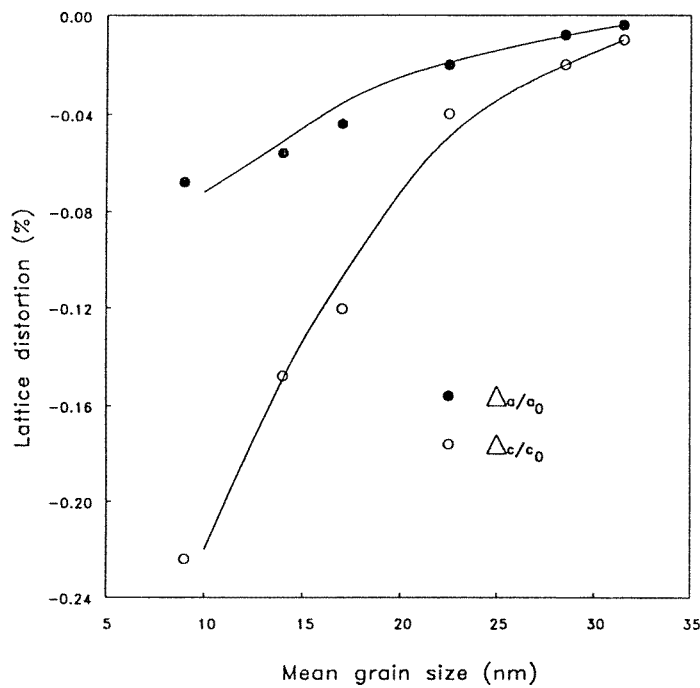
values of $\Delta a/a_0$ and $\Delta c/c_0$ are negative for the nanoscale Sn particles; the absolute values of $\Delta a/a_0$ and $\Delta c/c_0$ increase with decreasing grain size. When the mean grain size reduces to 9.2 nm, $\Delta a/a_0$ is as much as -0.07% and $\Delta c/c_0$ is as much as -0.22% . We observe similar results from figure 6: the variations of $\Delta a/a_0$ and $\Delta c/c_0$ for the nanoscale Bi particles are more remarkable. When the mean grain size is equal to 8.9 nm, $\Delta a/a_0$ is about -0.11% and $\Delta c/c_0$ is about -0.44% .

Table 1. Lattice parameters a and c , and unit cell volume V , of nanometre-sized Sn particles with different grain sizes.

Sample	A	B	C	D	E	F
$d_{(312)}$ (nm)	9.2	14	17	22.5	28.5	31.8
a (nm)	0.58270	0.58277	0.58284	0.58298	0.58304	0.58309
c (nm)	0.31749	0.31773	0.31782	0.31807	0.31814	0.31817
V (nm ³)	0.10780	0.10791	0.10796	0.10810	0.10815	0.10818

Table 2. Lattice parameters a and c , and unit cell volume V , of nanometre-sized Bi particles with different grain sizes.

Sample	A	B	C	D	E	F
$d_{(202)}$ (nm)	8.9	13.2	16.8	21.6	26.9	33.2
a (nm)	0.45410	0.45429	0.45446	0.45450	0.45456	0.45459
c (nm)	1.18078	1.18252	1.18412	1.18483	1.18532	1.18571
V (nm ³)	0.21086	0.21135	0.21180	0.21196	0.21210	0.21220

**Figure 5.** The variation of lattice distortions $\Delta a/a_0$ and $\Delta c/c_0$ with the mean size of nanometre-sized Sn particles.

The decreases in the lattice parameters result in reduced volume of the unit cell of the nanoscale particle. We have used $(V - V_0)/V_0$ to stand for the variation of the unit cell volume with a decrease in mean grain size, where V and V_0 are the unit cell volume of the nanoscale particles and the perfect single crystal respectively, as shown in figure 7 for Sn and figure 8 for Bi. It is clear from figures 7 and 8 that the variations of the unit cell volumes for both nanometre-sized Sn and Bi particles are always negative values; moreover, the smaller the

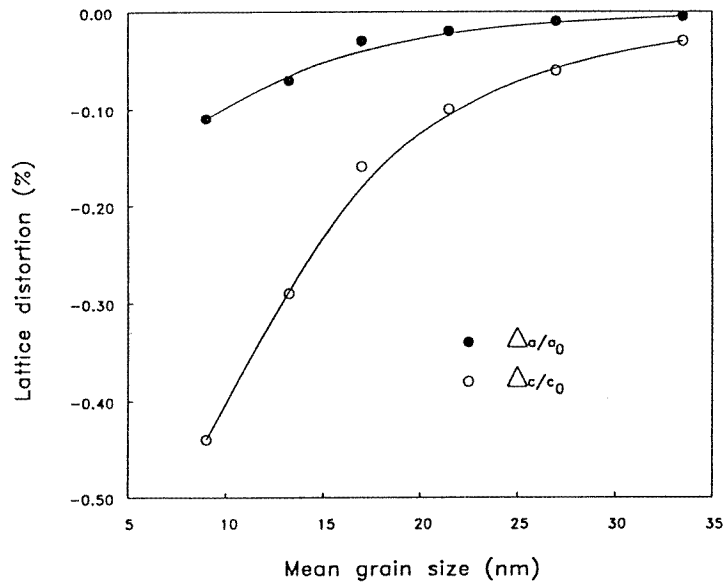


Figure 6. The variation of lattice distortions $\Delta a/a_0$ and $\Delta c/c_0$ with the mean size of nanometre-sized Bi particles

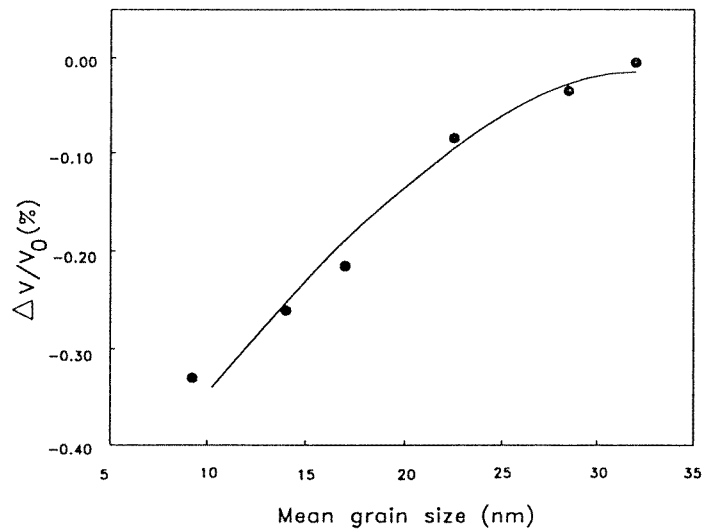


Figure 7. The relationship between the cell volume change $\Delta V/V_0$ and the mean grain size for nanometre-sized Sn particles.

grain sizes are, the larger the absolute values of $\Delta V/V_0$ are. For Sn, when the mean grain size is 9.2 nm, the value of $\Delta V/V_0$ is about -0.36% . For Bi, when the mean grain size is 8.9 nm, the value of $\Delta V/V_0$ is about -0.66% . Thus, lattice contractions for nanometre-sized particles of both Sn and Bi are obtained, and the contraction for a known mean particle size is greater in Bi than in Sn.

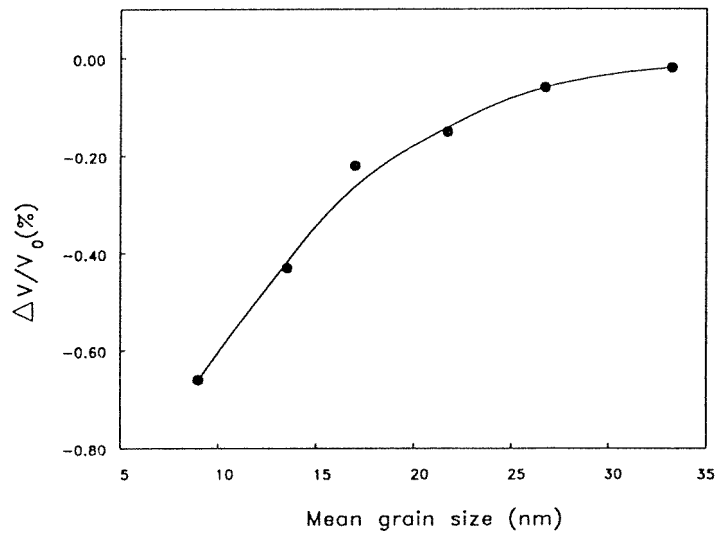


Figure 8. The relationship between the cell volume change $\Delta V/V_0$ and the mean grain size for nanometre-sized Bi particles.

4. Discussion

The EHD technique utilizes intense electric field to generate charged liquid droplets directly from the liquid state [12]. Under vacuum conditions, the droplets are disrupted again and accelerated by the electric field to a collector and will solidify in flight to produce particles. Because interactions with moulds, substrates or other particles are practically absent, and the active nucleation catalysts can be isolated into a small fraction of the total volume, the liquid droplets could achieve high undercoolings prior to nucleation. The concentration of vacancies in the rapidly solidified metal is larger than that in the metal as cast. The formation energy for the vacancy is smaller in the liquid metal than in the solid metal: for example, the formation energy for the vacancy in solid Al is 0.76 eV, and that in liquid Al is 0.11 eV [13]. The vacancy concentration in the liquid metal is therefore much higher than that in the solid metal. During the rapid solidification, most vacancies cannot separate in time and thus stay in the solid metal. In addition, because of the higher solidification velocity, it is easy for vacancies to form in the process of crystal growth. Therefore, there is much higher vacancy concentration in the nanometre-sized particles formed by rapid solidification. On the other hand, a reduction of grain size will enlarge the free energy of the crystallites and then raise the equilibrium solute solubility in the crystal lattice [14]. The enhanced solubility $\Delta C(T, D)$ can be expressed as the Gibbs–Thomson equation [15]:

$$\Delta C(T, D) = \frac{4\Omega\gamma C_0}{kTD} \quad (2)$$

where Ω is the atomic volume, γ the interfacial free energy, C_0 the equilibrium solute solubility in the coarse crystal, k the Boltzmann constant and D the grain size. In a pure element system, vacancies are the possible ‘solute atom’, thus supersaturated vacancies exist in the nanometre-sized particles. In a single crystal system, the vacancies may only exist in the point lattice sites. Consequently, a vacant lattice site solid solution is formed. The lattice parameters decrease with increasing number of vacant lattice sites in the solid solution, which leads to the lattice

contraction. The nanometre-sized particles produced by the EHD technique are found to be single crystals [16]. For Sn and Bi, the smaller the liquid droplets disrupted are, the faster the solidification velocities are, and the smaller the grain sizes are. Thus, according to the analyses above, there exist highly supersaturated vacancies in the point lattice sites for the nanoscale particles. This results in enhanced lattice contraction with a decrease in grain size of the nanoscale particles.

5. Conclusions

(i) Nanometre-sized Sn and Bi particles were produced by the electrohydrodynamic technique. The lattice parameters a and c for nanoscale Sn and Bi particles are all below the equilibrium values a_0 and c_0 of the Sn and Bi perfect single crystals respectively. With a decrease in grain size, the lattice parameters a and c reduce and the lattice contractions increase for both the nanometre-sized Sn and Bi particles.

(ii) The lattice contraction of nanometre-sized particles is explained by a supersaturation of vacant lattice sites in the nanoscale particles formed during rapid solidification and due to decreasing grain size.

Acknowledgment

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